

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
21 October 2004 (21.10.2004)

PCT

(10) International Publication Number
WO 2004/089622 A1

(51) International Patent Classification⁷: **B32B 27/08, 3/00**

(21) International Application Number:
PCT/GB2004/001560

(22) International Filing Date: 8 April 2004 (08.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0308028.0 8 April 2003 (08.04.2003) GB

(71) Applicant (for all designated States except US): **UNIVERSITY OF WARWICK** [GB/GB]; Gibbet Hill Road, Coventry CV4 7AL (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SMITH, Gordon, Frederick** [GB/GB]; 31 Myton Crescent, Warwick CV34 6QA (GB). **KIRWAN, Kerry, Emmett, Arthur** [GB/GB]; 32 Stanway Raod, Earlsdon, Coventry CV5 6PJ (GB).

(74) Agents: **BARNFATHER, Karl, Jon et al.**; Withers & Rogers, Goldings House, 2 Hays Lane, London SE1 2HW (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

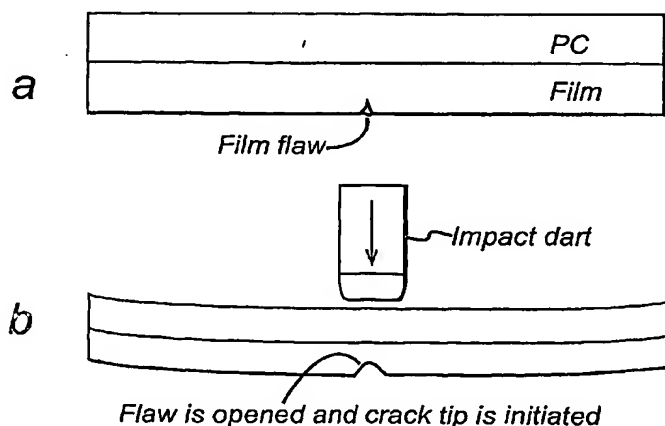
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LAMINATE MATERIAL



(57) Abstract: A laminate material comprising two components, a first thermoplastic polymer substrate and a second thermoplastic polymer blown film; wherein the film and substrate are directly bonded one to another and where substantially one face or side of the substrate only is laminated with film; such that in use the resistance of the substrate to a localised impact on a non-laminated face is significantly reduced by the presence of the film layer.

WO 2004/089622 A1

2/PRK

JCO5 Rec'd PCT/PTO 11 OCT 2005

PCT/GB2004/001560

10/552726

Laminate Material

This invention relates to a laminate material made from thermoplastic polymers the impact strength of which depends upon the direction of impact; and to a method of making such a material.

Thermoplastic polymer materials are widely used in manufactured goods. Some such materials ; such as polycarbonates are very tough and are used extensively in the manufacturing industries. For example; polycarbonates are used for glazing applications where they have been found to provide excellent intruder resistance. However, in such applications the use of such a tough material hinders escape in an emergency; for example, from a crashed vehicle. There is therefore a need for materials that exhibit directional impact properties; that is varying strength on each face; for example, in sheet form such a material may be broken more easily by impacting the inner face than by impacting the outer face. Thus, vehicle glazing made of such a material could be relatively easy to break from the inside while retaining its normal strength in respect to outside impacts.

It is an object of this invention to provide a laminate thermoplastic polymer material with directional impact properties. It is a further object to provide a method for manufacturing such a material where the degree of weakness on a selected face can be controlled by appropriate selection of manufacturing process conditions.

In one aspect the invention is a laminate material comprising two components, a first thermoplastic polymer substrate and a second thermoplastic polymer film; wherein the film and substrate are directly bonded one to another and where substantially one face or side only of the substrate is laminated with film; and the film has many small flaws generated as a result of the manufacturing process such that in use the resistance of the substrate to a localised impact on a non-laminated face is significantly reduced by the presence of the flaws in the film layer.

In another aspect the invention is a laminate material comprising two components, a first thermoplastic polymer substrate and a second thermoplastic polymer blown film; wherein the

film and substrate are directly bonded one to another and where substantially one face or side of the substrate only is laminated with film; such that in use the resistance of the substrate to a localised impact on a non-laminated face is significantly reduced by the presence of the film layer. Preferably the polymer blown film is impact modified.

In a further aspect the invention comprises a method of making the above laminate material where thermal bonding is used to directly bond a first thermoplastic polymer substrate and a second thermoplastic impact modified polymer blown film. Preferably, the directional impact properties of the material are controlled by adjusting the strength of the thermal bonding. The temperature and/or pressure applied to bond the film and substrate may be varied in order to adjust the strength of the thermal bonding. Preferably, the thermoplastic polymer substrate is a polycarbonate material and the thermoplastic impact modified polymer blown film is a highly rubberised blown acrylic film. The thickness of the blown film may be between 50 and 250 μm and is preferably about 100 μm .

Typically, the material may be manufactured in sheet form. However, the invention may also be used where the material is shaped and has varying thickness; for example a vehicle windscreen. The material of the invention may optionally have added weathering materials or colouring agents.

The material of the invention has many advantageous safety applications; for example, glazing windows and partitions in vehicles and also domestic/commercial applications such as glazing in windows or showers enclosures in the home; where escape in an emergency is an important issue.

The invention will now be described by reference to the following figures;

Figure 1 shows schematically the main features of known apparatus used for manufacturing blown film;

Figures 2a and 2b show schematically a laminated sheet according to the invention before and during a localised impact; and

Figure 3 is a bar chart that shows the impact resistance of unlaminated polycarbonate sheet material, and laminated polycarbonate sheet material (from both sides) prepared according to the method of the invention described in Example 1.

In order to achieve the desired directional impact properties it has been found that it is much preferred to use a blown film/layer. However, a layer produced by other means such as simple extrusion may also be used provided that many small surface flaws are present. Preferably, blown film is impact modified; that is it has been toughened, typically by adding rubberising agents. In the film blowing process (see Figure 1) plastic melt passes through an extruder (E) and a die (T) - that forms it into an annular shape, usually directed upwardly. A molten plastic tube emerges from the die and this is subjected to both a moderate internal air pressure generated by process air introduced via an air inlet (A), and a longitudinal force via take-off rolls (R'). The tube is cooled by air from an external air ring (R). Under these conditions the molten tube gradually expands into a larger diameter stable solid cylindrical "bubble" beyond the 'freeze' line (F). The bubble is gradually flattened in a collapsing device (C), which consists of a pair of converging, ladder-like sets of idler rolls, and thereafter by the take-off rolls (R') where it is handled as a thin flat film.

It has been found that blown film has many small flaws in its surface. These flaws play a vital role in achieving the object of the invention. When the non-laminated side of a material laminated according to the invention suffers a localised impact of sufficient intensity the surface of the film is put into tension (see Figures 2a and 2b) upon impact and flaws present in surface of the blown film, especially in the locality of the impact, will open to form a crack. A crack may be initiated at a very low energy level and the crack will then propagate backwardly first through the film and then to through the directly bonded substrate, with relative ease.

In simple terms, the blown film 'tears' easily in tension and the crack then propagates rapidly through the sample, causing brittle failure. This effect is most pronounced for localised impacts (as produced by sharp objects). If the impact is from a blunt object it will normally be spread over a larger area, and failure will not occur so readily. This property is particularly advantageous for glazing applications, where a single blow by a key/stiletto heel/hammer is

likely to induce failure, but a blow from an elbow or head would not. Thus, safety would not be compromised during an accident, but escape would be assisted after an accident.

It has been found most advantageous to employ an impact modified material for the blown film; typically a highly rubberised acrylic blown film. During a low energy level impact on the film face, the surface of the highly rubberised film is put into a compressive state by the impacting object and any flaws are effectively closed. A crack in the blown film is not initiated until a medium-to-high energy level is reached due to the cushioning effect of the compressed rubber molecules. The use of an impact modified blown film material, rather than simply a blown film material, advantageously results in the impact strength of the film face up side of the material being only marginally less than substrate alone (un-laminated material).

For a crack to progress through a medium it has to have sufficient energy at the crack tip to propagate. There must also be a continuing medium for the crack to travel through, i.e. good adhesion at the interface. If there is not good adhesion at the interface then delamination may occur; the crack tip is blunted and cannot continue through the sample. This phenomenon is known as 'film-debonding' and is caused by low interface toughness compared to that of the film and the substrate.

The following Examples detail methods for producing a sheet of material according to the invention. While in Examples 1 and 2 injection moulding was used to thermally bond the substrate and the blown film it has been found that other laminating process can be used such as co-extrusion, calendering etc..

Example 1

Seven samples were manufactured using conventional injection moulding. A 'blown' impact modified rubberised acrylic film was laid in a mould cavity, comprising a simple flat plaque, measuring 150 mm x 150 mm x 3 mm, with a conventional runner and gate system. The film used was 100 μ m thickness and was supplied by Polymer Extruded Products, 297 Ferry Street, Newark, New Jersey 07105.

Molten Polycarbonate was back-injected onto the film. The polycarbonate grade was Bayer Makrolon AL2647 (supplied by Bayer GmbH, Germany). The process settings (see Table 1) were such that full mould fill and packing were obtained.

Finally, the samples were removed from the machine, the sprue and gates removed and then impact tested.

Table 1 - Process Data

Barrel Temperatures: 260° C to 280° C

Injection Temperature: 280 °C

Tool Temperature: 30 °C

Metering: - 92mm

Screw Speed: - 100rpm

Back Pressure: - 5 bar

Injection Speed: - 35 mm/s

Injection Pressure: - 175 bar

Changeover: - 5mm

Holding Time: - 15s

Holding Pressure: - 30 bar

Testing of Samples produced by Example 1

The samples produced via the method above were impact tested in two ways, the first with the film face up (i.e. film on the impact side) and secondly with the film face down (i.e. film opposite the impact face).

The impact tests used a Pneumatic Dart Impact machine equipped that complies with ASTM D3763-99 and a 12.5 mm radius hemispherical impact dart was used. The flat samples were placed in the clamp zone of the Dart Impact machine. When the safety door shuts the test pieces are hydraulically clamped in position. When the test is initiated the dart is fired downwards through the sample. The trials were conducted in accordance with ASTM D3763-99.

Three sets of samples were tested (see Table 1). Samples 1 to 7 relate to polycarbonate with no blown film laminate; Samples 8 to 14 relate to samples laminated according to the invention impacted upon the film face; and Samples 15 to 21 refers to samples laminated

according to the invention an impact tested on the non-film face. The samples were impacted using an initial dart height of 40 mm and an impact velocity of 4 ms^{-1} . A computer logged data for post-test analysis. For these data the total energy absorbed by the component before failure along with observations of the manner of failure, i.e. brittle or ductile was logged. Impact tests were also conducted with un laminated polycarbonate in order to provide a reference. The results are illustrated in Figure 3.

It can be seen that the blown film face up samples exhibited impact failure energy levels (58 Joules to 73 Joules) only slightly less than for un-laminated polycarbonate samples (73 Joules to 87 Joules) of similar dimension; both failing in a ductile manner. However, a significantly lower energy of 1.7 Joules to 6.1 Joules was required when the sample was impacted on the polycarbonate face side (film face down) and the samples failed in a brittle manner.

Similar experiments have also been undertaken with another commercial grade acrylic; Orogas DRT TM (available from Atofina - UK Head Office, Globe House, Bayley Street, Stalybridge, Cheshire SK15 1PY, United Kingdom)

It is believed that when a sample is impacted upon the film face, the film is placed into compression and any flaws effectively close and so do not initiate cracks and so the toughness and ductility of the polycarbonate is maintained.

Table 1 - Impact Strength Test Data

Sample Number	Impacted Upon	Peak Load (N)	Failure Mechanism	Total Energy Absorbed (J)
1	No Film	6519	Ductile	72.91
2	No Film	6860	Ductile	80.90
3	No Film	6875	Ductile	79.96
4	No Film	6947	Ductile	80.80
5	No Film	6926	Ductile	78.88
6	No Film	6675	Ductile	84.41
7	No Film	6800	Ductile	86.71
8	Film Face	6436	Ductile	63.57
9	Film Face	6403	Ductile	63.81
10	Film Face	6155	Ductile	57.89
11	Film Face	5616	Ductile	64.33
12	Film Face	6493	Ductile	72.50
13	Film Face	6070	Ductile	61.23
14	Film Face	6319	Ductile	67.66
15	Non Film Face	1048	Brittle	2.17
16	Non Film Face	663	Brittle	1.68
17	Non Film Face	1163	Brittle	4.89
18	Non Film Face	688	Brittle	1.78
19	Non Film Face	1433	Brittle	6.08
20	Non Film Face	998	Brittle	5.01
21	Non Film Face	904	Brittle	3.71

Example 2

By lowering the processing temperature of the polycarbonate material used for the substrate from 280° C to 260° C was found that it was possible to produce some samples that exhibited higher non film side impact strength than those discussed above, but still significantly lower than unlaminated polycarbonate components (see Table 2).

Closer inspection of the test pieces after impact testing revealed different failure characteristics. Firstly when impacted on the polycarbonate side samples failed in a ductile manner, similar to when the samples of Example 1 were impacted on the film side, and in contrast to the dramatic brittle 'explosion' failure observed for polycarbonate side tests undertaken (Example 1). Secondly, film in the area of the impact was severely stressed and de-laminated from the PC substrate in small pieces.

Thus, the level of energy required to induce failure can be increased or decreased by controlling the level of adhesion (direct bonding) between the film and the substrate; effectively using the film-substrate interface as a crack inhibitor. High interfacial adhesion means that the crack is able to propagate easily across the interface ; while low interfacial adhesion means that the crack has difficulty in crossing the interface as the film debonds from the substrate.

The interfacial strength of the thermal bond between the substrate and the blown film may be controlled by varying other process conditions such as injection temp, injection speed, holding pressure etc.

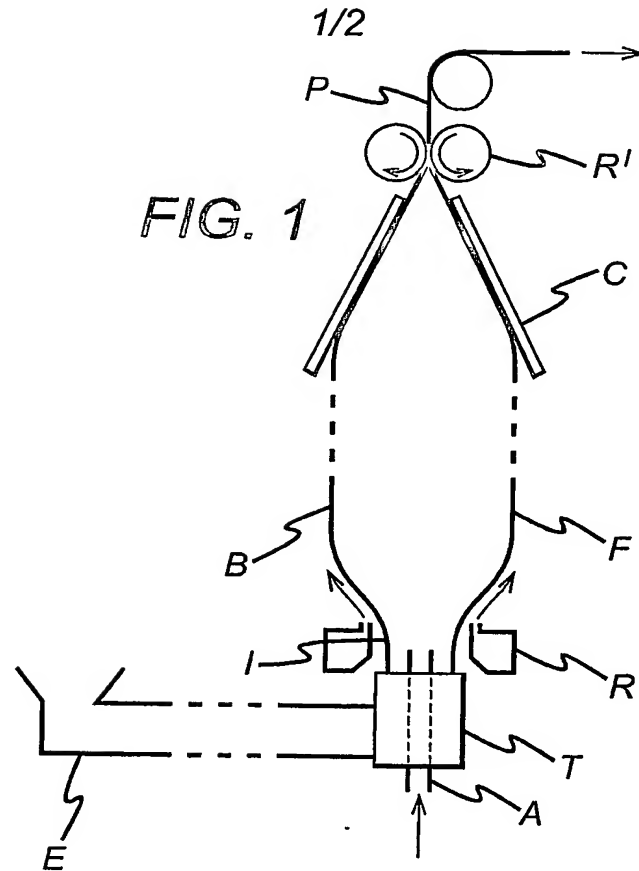
Table 2

Sample Number	Impacted Upon	Peak Load (N)	Total Energy Absorbed (J)
1	Non-Film Face	5627	42.06
2	Non-Film Face	5709	43.17
3	Non-Film Face	5490	41.24
4	Non-Film Face	5567	41.78
5	Non-Film Face	5740	43.30
6	Non-Film Face	5612	41.98
7	Non-Film Face	5730	43.22

CLAIMS

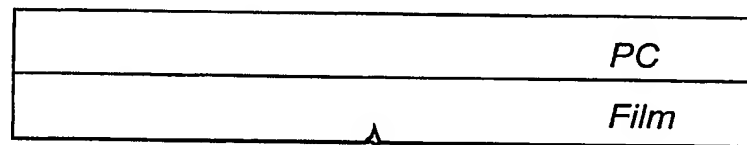
1. A laminate material comprising two components, a first thermoplastic polymer substrate and a second thermoplastic polymer film; wherein the film and substrate are directly bonded one to another and where substantially one face or side only of the substrate is laminated with film; and the film has many small flaws generated as a result of the manufacturing process such that in use the resistance of the substrate to a localised impact on a non-laminated face is significantly reduced by the presence of the flaws in the film layer.
2. A laminate material comprising two components, a first thermoplastic polymer substrate and a second thermoplastic polymer blown film; wherein the film and substrate are directly bonded one to another and where substantially one face or side of the substrate only is laminated with film; such that in use the resistance of the substrate to a localised impact on a non-laminated face is significantly reduced by the presence of the film layer.
3. A laminate material according to Claim 2 wherein the polymer blown film is impact modified.
4. A method of making a material according to any of Claims 1 or 3 where thermal bonding is used to directly bond the film and substrate.
5. A method according to Claim 4 wherein the directional impact properties of the material are controlled by adjusting the strength of the thermal bonding.
6. A method according to Claim 5 where the temperature and/or pressure applied to bond the film and substrate are varied in order to adjust the strength of the thermal bonding,
7. A method according to any of Claims 4 to 6 wherein the thermoplastic polymer substrate is a polycarbonate material.
8. A method according to any of Claims 4 to 7 wherein the film is a blown acrylic film.

9. A method according to any of Claims 4 to 8 wherein the film is between 50 and 250 μm thickness.
10. A method according to any of Claims 4 to 8 wherein the film is between 75 and 125 μm thickness.
11. A material made according to the method of any of Claims 4 to 10.
12. A material according to Claim 1, 2, 3 or 11 where the material is in the form of a sheet.
13. A laminate material comprising two components, a first layer and a second thermoplastic polymer layer, bonded to one another; the second layer having a lower resistance to a localised impact than the first layer, prior to bonding; but wherein an impact against the face of the first layer of the laminate enables breakage of the laminate material with a lower impact energy than that required to enable breakage of said first layer prior to bonding.



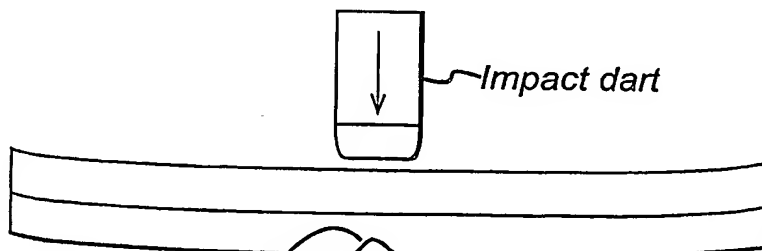
(E) Extruder (I) Molten Tube (B) Bubble (P) Product
 (R') Pinch/Take-off Rolls (C) Collapsing Device (F) Freeze Line
 (R) Cooling Air Ring (T) Tool (die) (A) Air Inlet

FIG. 2a



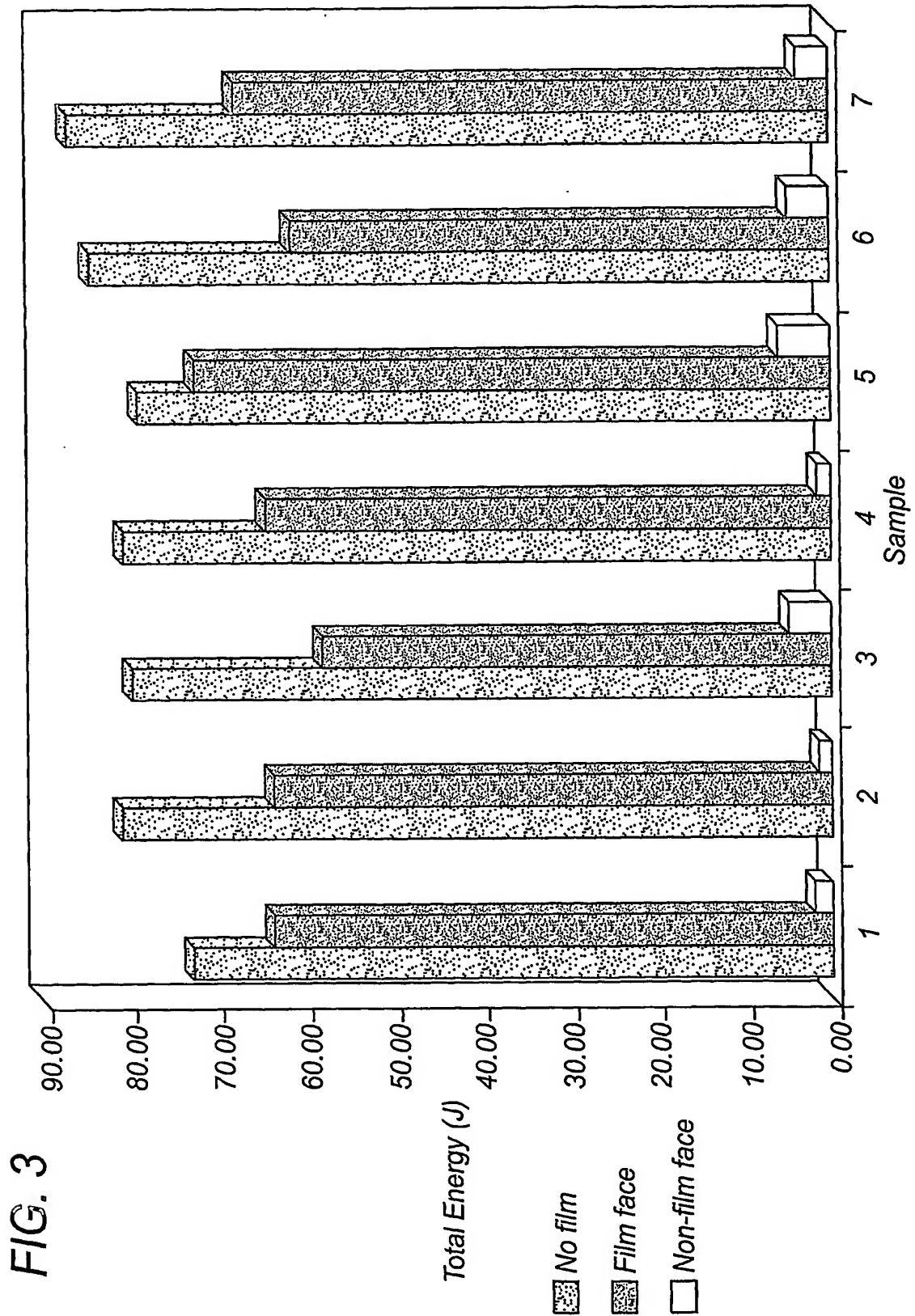
Film flaw

FIG. 2b



Flaw is opened and crack tip is initiated

2/2



INTERNATIONAL SEARCH REPORT

PCT/GB2004/001560

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B27/08 B32B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 022 311 A (MITSUBISHI RAYON CO) 26 July 2000 (2000-07-26) Acrylic film, possibly blown, which may be laminated to polycarbonate. page 2, line 33 - line 53 page 6, line 11 - line 20 page 7, line 35 - line 50 -----	1-13
X	EP 0 445 955 A (MITSUI PETROCHEMICAL IND ; SHELL OIL CO (US)) 11 September 1991 (1991-09-11) Blown acrylic film which can be laminated to a polycarbonate substrate. Packaging. page 2, line 35 - line 43 page 2, line 53 - page 3, line 1 page 3, line 42 - page 4, line 2 ----- -/-	1-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the International filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the International filing date but later than the priority date claimed

T later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the International search

15 July 2004

Date of mailing of the International search report

26/07/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Stinchcombe, J

INTERNATIONAL SEARCH REPORT

PCT/GB2004/001560

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 5 763 062 A (BOLTON NELSON ET AL) 9 June 1998 (1998-06-09) Blown acrylic ionomer film laminated to polycarbonate. Used in laminated glass. column 2, line 57 - line 59 column 4, line 55 - column 5, line 7 column 6, line 44 - line 48</p>	1-13
X	<p>US 4 668 574 A (BOLTON NELSON P ET AL) 26 May 1987 (1987-05-26) Laminate for safety glass comprising polycarbonate and acrylic-containing ionomer. column 4, line 33 - line 41 column 5, line 19 - line 48</p>	1,4-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB2004/001560

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1022311	A	26-07-2000	JP 3433892 B2	04-08-2003
			JP 11080487 A	26-03-1999
			DE 69809788 D1	09-01-2003
			DE 69809788 T2	14-08-2003
			EP 1022311 A1	26-07-2000
			US 6509097 B1	21-01-2003
			CN 1136266 B	28-01-2004
			WO 9914272 A1	25-03-1999
EP 0445955	A	11-09-1991	US 5066543 A	19-11-1991
			AT 153361 T	15-06-1997
			AU 642966 B2	04-11-1993
			AU 7139891 A	29-08-1991
			CA 2037321 A1	29-08-1991
			DE 69126154 D1	26-06-1997
			DE 69126154 T2	25-09-1997
			EP 0445955 A2	11-09-1991
			JP 4211442 A	03-08-1992
			KR 185989 B1	15-05-1999
			NO 910769 A	29-08-1991
			NZ 237246 A	28-07-1992
US 5763062	A	09-06-1998	NONE	
US 4668574	A	26-05-1987	CA 1243590 A1	25-10-1988
			DE 3486336 D1	22-09-1994
			DE 3486336 T2	23-03-1995
			EP 0140969 A1	15-05-1985
			JP 5030621 B	10-05-1993
			JP 60501201 T	01-08-1985
			WO 8404277 A1	08-11-1984
			US 4663228 A	05-05-1987